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PRIMARY SOURCES AND TOXICITY OF PAHS IN MILWAUKEE-AREA STREAMBED SEDIMENT

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Abstract: High concentrations of polycyclic aromatic hydrocarbons (PAHs) in streams can be a significant stressor to aquatic organisms. To understand the likely sources and toxicity of PAHs in Milwaukee-area streams, streambed sediment samples from 40 sites and parking lot dust samples from 6 sites were analyzed for 38 parent PAHs and 25 alkylated PAHs. Diagnostic ratios, profile correlations, principal components analysis, source-receptor modeling, and mass fractions analysis were used to identify potential PAH sources to streambed sediment samples, and land-use analysis was used to relate streambed sediment PAH concentrations to different urban-related land uses. On the basis of this multiple lines-of-evidence approach, coal-tar pavement sealant was indicated as the primary source of PAHs in a majority of streambed sediment samples, contributing an estimated 77% of total PAHs to samples, on average. Comparison with the probable effect concentrations and (or) the equilibrium partitioning sediment benchmark indicates that 78% of stream sediment samples are likely to cause adverse effects to benthic organisms. Laboratory toxicity tests on a 16-sample subset of the streambed sites using the amphipod *Hyalella azteca* (28-d) and the midge *Chironomus dilutus* (10-d) measured significant reductions in 1 or more biological endpoints, including survival, in 75% of samples, with *H. azteca* more responsive than *C. dilutus*. *Environ Toxicol Chem* 2016;9999:1–14. © 2016 The Authors. Environmental Toxicology and Chemistry Published by Wiley Periodicals, Inc. on behalf of SETAC.

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INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are widespread contaminants in urban aquatic sediments and typically occur as complex mixtures [1,2] with numerous natural and anthropogenic sources. Polycyclic aromatic hydrocarbons are categorized as either petrogenic or pyrogenic: petrogenic PAHs form at low temperatures over geologic time scales, whereas pyrogenic PAHs form rapidly at high temperatures during incomplete combustion of carbon-based material. Sources of petrogenic PAHs include fossil fuels such as unprocessed coal and crude and refined petroleum products (gasoline, diesel, motor oil, home heating oil, lubricants, and asphalt) [3]. Pyrogenic PAHs come from natural sources, such as forest and grass fires and volcanic eruptions, and from anthropogenic sources, such as gasoline- and diesel-engine exhausts, coal-fired power plant emissions, coke-oven emissions, residential wood burning, creosote, and coal tar from legacy manufactured gas plants and pavement sealants [2–4].

Polycyclic aromatic hydrocarbons are transported to streams and lakes via atmospheric deposition; industrial and wastewater discharges; and runoff from surfaces such as streets, parking lots, and rooftops [4,5]. Most PAHs are hydrophobic and thus sorb to suspended particulates in the water column and subsequently precipitate and accumulate in streambed and lakebed sediments. Some PAHs are toxic, carcinogenic, mutagenic, and (or) teratogenic and can therefore be detrimental to aquatic organisms [6]. Sediment contaminated with PAHs can also pose an economic burden to communities charged with contamination clean-up. Communities in the area of Minneapolis–St. Paul (MN, USA) estimate that the disposal cost of dredged sediment from storm water ponds will reach $1 billion, because elevated PAH concentrations in the sediment—chiefly from coal-tar–based pavement sealant—require disposal in specially lined landfills [7]. In the Great Lakes region (USA), more than $500 million has been spent since 2002 at 19 different sites to clean up contaminated sediment, with a primary focus on polychlorinated biphenyls and PAHs [8].

A recent study of streams in the area of Milwaukee (WI, USA) found that, among 15 classes of organic contaminants, PAHs posed the greatest risk to aquatic organisms [9]. The present study provides a more comprehensive assessment of the potential toxicity of sediment-associated PAHs to benthic aquatic organisms in Milwaukee-area streams by comparing PAH concentrations in streambed sediment samples with sediment quality guidelines and through laboratory toxicity tests. In addition, a multiple-lines-of-evidence approach is used to determine the most important sources of PAHs to Milwaukee-area streambed sediment. Individually, each diagnostic method used in the present study has limitations and uncertainties. By using a multiple-lines-of-evidence approach, the uncertainties of each method are mitigated, and common conclusions are strengthened [10,11]. The diagnostic methods used for identification of PAH sources were land-use analysis [12], ratios of parent to alkylated PAHs [2], ratios of high molecular weight to low molecular weight PAHs [7], diagnostic ratios of

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compound pairs [13], PAH profiles [14], principal components analysis [15], the US Environmental Protection Agency (USEPA) Chemical Mass Balance (CMB) 8.2 receptor model [7], and mass fraction analysis [16].

METHODS

Site selection

Samples were collected during summer 2014 from 40 streambed and 6 parking lot sites in the Milwaukee area (Figure 1; Supplemental Data, Table S1). The streambed sites were selected to represent watersheds with a range of urban land uses: residential, commercial, industrial, transportation (roads and streets), parking, and other urban uses. Combined, these urban land uses make up 14% to 99% of each watershed (median, 81%; Supplemental Data, Table S1). Drainage areas to each watershed ranged from 0.3 km^2 to 2239 km^2, and stream characteristics such as depth, turbidity, and canopy cover varied widely. Upland soils are glacial in origin and dominated by sand loams, silt loams, and clay loams [17]. Streambeds were low

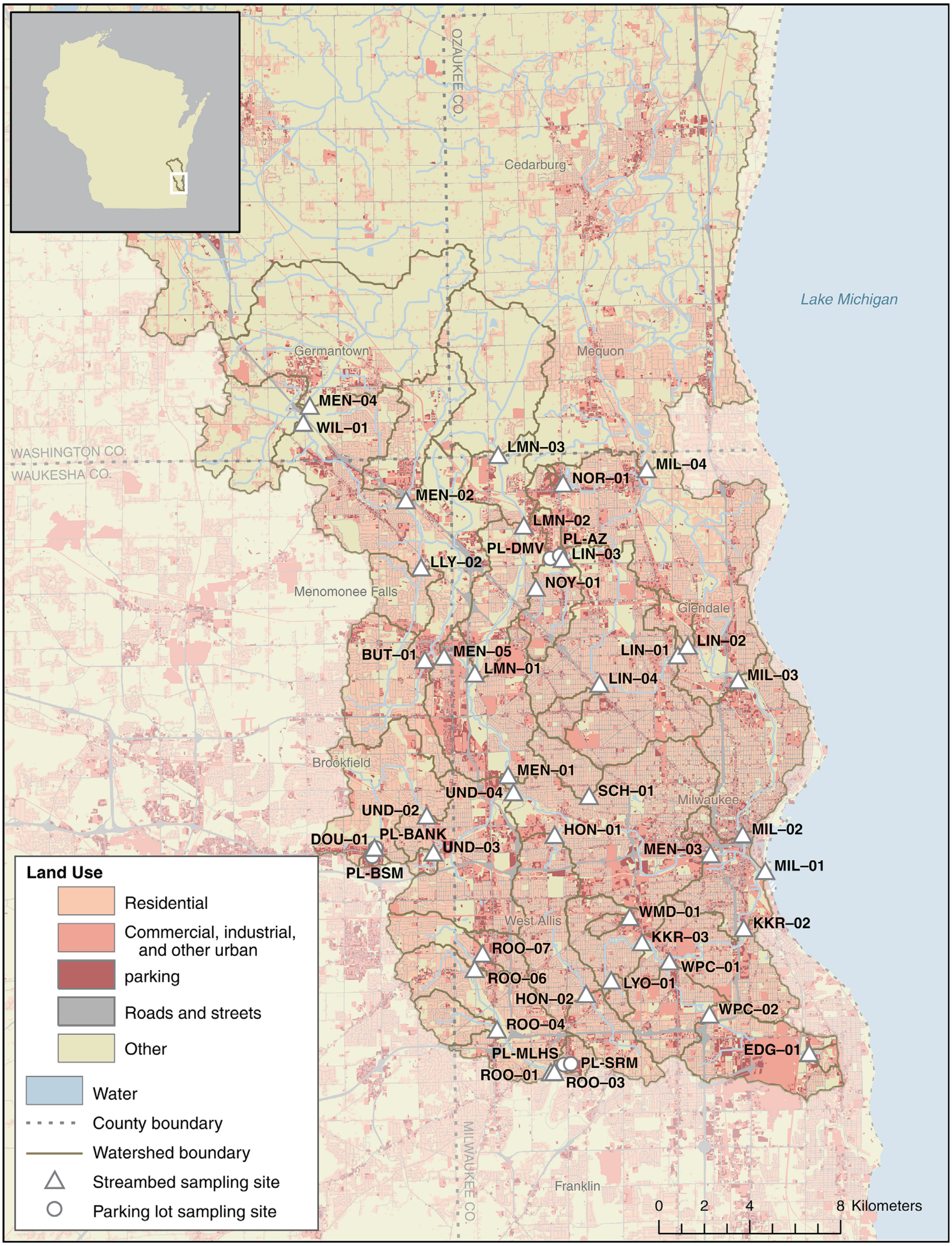

Figure 1. Map of sampling sites. Land-use data from Southeastern Wisconsin Regional Planning Commission (SEWRPC) detailed 2010 Land Use Inventory [33]. Site abbreviations are defined in Supplemental Data, Table S1.

gradient with a large variation in composition from cobbles to fine sediments. Area parking lots were sampled for comparison with other studies, which have found parking lot pavement sealants to be a primary source of PAHs to streams [7,13], and for comparison with streambed sediment samples. Parking lot sites were selected based on composition (concrete or asphalt) and sealed status (sealed or unsealed), broad geographic distribution spanning the stream sampling area, and close proximity (as close as 100 m) to 1 or more sampled streambed sites.

Sample collection and analysis

Sample collection methods are detailed in the Supplemental Data. To summarize, streambed sediment—composed mostly of silt, but also clay and sand—was composited from the upper 25 mm to 50 mm in multiple depositional areas at each site. Parking lot dust and particulates were collected by using a stainless steel vacuum. Following collection, all samples were stored in the dark at 4 °C and shipped, on ice, to the US Geological Survey (USGS) National Water Quality Laboratory in Denver, Colorado. Environmental duplicates were collected at 2 sites (LIN-01 and PL-BANK), with a median relative percentage difference of 11.5%. Environmental and laboratory quality-control samples are further discussed in the Supplemental Data.

Samples were analyzed for 38 parent and 25 alkylated PAHs by the USGS National Water Quality Laboratory (NWQL analytical schedules 5506 and 5507; Supplemental Data, Table S2). Including alkylated compounds enabled computation of ratios of parent to alkylated compounds, a useful source identification method that is not possible if analysis is limited to the 16 EPA Priority Pollutant PAHs (Supplemental Data, Table S2). Laboratory analytical methods are described in detail in Zaugg et al. [18], and are summarized in the present study. Surrogate compounds were added to each sample prior to extraction using water/isopropyl alcohol. Compounds of interest were isolated from the water/isopropyl alcohol extracts by using polypropylene solid-phase extraction (SPE) cartridges followed by elution with a mixture of dichloromethane (DCM) and diethyl ether (DEE). The DCM–DEE eluent was further cleaned up by passing through a sodium sulfate/Florisil® SPE cartridge. The extract volume was reduced to 500 μL, and internal standards were added. The extracts were analyzed by capillary-column gas chromatography/mass spectrometry.

Laboratory reporting levels varied by compound and by sample. The default reporting levels of parent and alkylated compounds were 0.025 mg/kg and 0.05 mg/kg, respectively. However, reporting levels were often scaled up because sample extracts had to be diluted or because sample weights were below the default 10 g (reporting levels were scaled by sample weight). The median adjusted reporting level of parent compounds was 0.27 mg/kg, with a maximum of 3.03 mg/kg, and the median adjusted reporting level of alkylated compounds was 0.55 mg/kg, with a maximum of 3.98 mg/kg (Supplemental Data, Figure S1). Nondetections made up 10% of results for the 16 USEPA Priority Pollutants, 46% of results for the alkylated compounds, and 35% of the total results. Zeros were used as conservative substitutes for nondetections in summations of total sample concentrations (ΣPAH_{16}). Samples with nondetections were excluded from diagnostic ratios, PAH profiles, principal component analysis, and the CMB model.

Toxicity assessment using sediment quality guidelines

Potential toxicity of streambed sediments to aquatic organisms was assessed by using comparisons with the following sediment quality guidelines: the probable effect concentration (PEC), the threshold effect concentration (TEC), and the sum equilibrium-partitioning sediment benchmark toxicity unit (ΣESBTU). The PEC (22.8 mg/kg for ΣPAH_{16}) is the concentration above which adverse effects on aquatic organisms are likely; the TEC (1.61 mg/kg for ΣPAH_{16}) is the concentration below which adverse effects are unlikely [19,20]. The PEC quotients (PECQs) and TEC quotients (TECQs) were computed for each sample by dividing the ΣPAH_{16} concentration in the sample by the PEC and TEC, with adverse effects to benthic organisms predicted at PECQs greater than 1.0 and unlikely at TECQs less than 1.0 [19].

The ΣESBTU approach accounts for the biological availability of individual PAH compounds in a mixture, and is applicable across sediment types [21]. To compute the ΣESBTU, total organic carbon (TOC)-normalized concentrations of 37 PAHs were divided by compound-specific final chronic values and summed. Streambed sediments with ΣESBTUs less than 1.0 are expected to be nontoxic to benthic organisms, whereas sediments with ΣESBTUs greater than 1.0 are expected to have adverse effects.

Toxicity assessment using laboratory toxicity tests

Laboratory toxicity tests (i.e., bioassays) on a subset of 16 streambed sediment samples (Supplemental Data, Table S1) were conducted at the USGS Columbia Environmental Research Center (Columbia, MO; details of the toxicity tests are provided in the Supplemental Data). Two control sediments were also tested: Spring River sediment [22,23] and quartz sand [24]. Individual PAH compound concentrations of the control sediments were below the reporting level of 0.02 mg/kg. Two species were tested: the midge *Chironomus dilutus* and the amphipod *Hyalella azteca*. Duration of the exposures was 10 d for midges and 28 d for amphipods. Endpoints measured were amphipod survival, dry weight (estimated from length), and biomass; and midge survival, ash-free-dry weight (AFDW), and biomass. Surviving amphipods at the end of the 28-d sediment exposure were exposed for 4 h to 7.5 $\mu W/cm^2$ ultraviolet (UV as UVB) light to evaluate the phototoxicity of PAHs accumulated by amphipods. The light intensity was selected to be representative of levels of UV light in aquatic environments [25,26]. Survival and mobility of amphipods at the end of the UV light exposure were evaluated, and organisms were preserved for length measurements. Survival was established based on movement observed during a 5-s observation period after organisms were gently prodded with a pipette. Immobility was established based on the observation of surviving organisms exhibiting lethargic movement (e.g., lack of active swimming after prodding with a pipette).

Statistical analyses of toxicity endpoints were done in accordance with guidelines of the USEPA [27] and the ASTM International [28,29]. Differences in toxicity endpoints relative to control sediments were determined by analysis of variance (ANOVA) with mean separation by Duncan's multiple-range test at $p < 0.05$. Statistical analyses were conducted by using 1-way ANOVA at $p = 0.05$ for all endpoints except length, which was analyzed with a 1-way nested ANOVA at $p = 0.05$ (amphipods nested within a beaker [30]). Before statistical analyses were performed, all data were tested for normality.

Data for endpoints that were not normally distributed were either transformed with arcsin transformation (survival) or log-transformation (length, weight, biomass), or converted to ranks (if the endpoint data were heterogeneous) before statistical analysis. Regression curves displayed in pairwise graphs between endpoints and computed PECQs and ΣESBTUs were fit with 3-parameter log-logistic models using the drm function from the drc package in the R statistical computing software [31].

Watershed land use

A geographic information system (GIS) was used to generate watershed boundaries with Esri's geoprocessing service, Watershed, accessible through ArcGIS Online [32]. Digital elevation data used by the tool were at a resolution of 30 m. Boundaries were compared with digital topographic maps and aerial imagery, and any issues encountered were corrected manually. Corrected boundaries were used to summarize land-use data for each site by using data from the Southeastern Wisconsin Regional Planning Commission (SEWRPC) detailed 2010 Land Use Inventory [33]. The SEWRPC land-use codes were grouped into land-use categories as follows: residential (100s), commercial (200s), industrial (300s), roads and streets (411–418G), parking (425–437), other urban (441–712), natural areas (731–799 and 910–950), and agriculture (811–871).

Identification of PAH sources

Land-use analysis. Relations between different urban land uses and streambed sediment ΣPAH_{16} concentrations were assessed by using Spearman correlation with a significance level (p value) of 0.05.

Parent/alkylated and high molecular weight/low molecular weight compounds. Ratios of parent and alkylated PAHs were used to differentiate between petrogenic (generally dominated by alkylated compounds) and pyrogenic (generally dominated by parent) PAHs [2]. The parent compounds were anthracene, benz[*a*]anthracene, benzo[*a*]pyrene, benzo[*e*]pyrene, chrysene, fluoranthene, naphthalene, perylene, phenanthrene, and pyrene; alkylated compounds were the C1 to C4 alkylated forms of the parents. In addition, ratios of low molecular weight (2–3 ring) and high molecular weight (>3 ring) PAHs (Supplemental Data, Table S2) were used to differentiate between petrogenic PAHs (generally dominated by low molecular weight compounds) and pyrogenic PAHs (generally dominated by high molecular weight compounds) [7].

Diagnostic ratios. Different PAH sources are often characterized by diagnostic ratios (called ratios hereafter) of particular compounds, which can be used for PAH source identification [2,4,13]. The following ratios were computed for samples and compared with source ratios from the literature: anthracene/(anthracene+phenanthrene), fluoranthene/pyrene, fluoranthene/(fluoranthene+pyrene), benz[*a*]anthracene/(benz

Table 1. Polycyclic aromatic hydrocarbon (PAH) sources used in diagnostic methods

PAH source category	PAH source (abbreviation) [reference]	Method	PAH source (abbreviation) [reference]	Method
Petrogenic	Kerosene (KERO) [13]	DR	Lubricating oil (LOIL) [13]	DR
	Diesel oil (DOIL) [13]	DR	Coal (COA1) [13]	DR
	Crude oil (CRU1) [13]	DR	Coal (COA2) [2]	DR
	Crude oil (CRU2) [2]	DR	Asphalt (ASP1) [13]	DR
	Shale oil (SHAL) [13]	DR	Asphalt (ASP2) [34]	P
Coal comb.	Power plant emis. (PPLT) [34]	P	Hard coal briquette comb. (CCB4) [13]	DR
	Coal average (CCB1) [34]	P	Residential heating (RESI) [34]	P
	Lignite and brown coal comb. (CCB2) [13]	DR	Coke oven emis. (COKE) [34]	P
	Bituminous coal comb. (CCB3) [13]	DR		
Vehicle related	Diesel vehicle particulate emis. (DVEM) [34]	P	Vehicle/traffic average (VAVG) [34]	P
	Diesel comb. (DCOM) [13]	DR	Tire particles (TIRE) [34]	P
	Gasoline vehicle particulate emis. (GVEM) [34]	P	Used motor oil #1 (UMO1) [34]	P
	Gasoline comb. (GCOM) [13]	DR	Used motor oil #2 (UMO2) [34]	P
	Traffic tunnel air (TUN1) [34]	P	Used engine oil, gas vehicle (UEOG) [13]	DR
	Roadway tunnels (TUN2) [13]	DR	Used engine oil, diesel vehicle (UEOD) [13]	DR
Urban background	Road dust (ROAD) [13]	DR	Urban air (URBN) [13]	DR
Plant comb.	Pine wood soot particles #1 (PIN1) [34]	P	Wood comb. (WDCB) [13]	DR
	Pine wood soot particles #2 (PIN2) [7]	P	Grasses comb. (GRAS) [13]	DR
	Oak wood soot particles (OAKS) [7]	P	Bush fire (BUSH) [13]	DR
	Wood soot (WDST) [13]	DR	Savanna fire particulate (SAVA) [13]	DR
Coal tar	Coal-tar-sealed pavement dust, 6-city avg. (CTD6) [34]	DR, P	Coal tar product (CTR1) [2]	DR
	Coal-tar–sealed pavement dust, 7-city avg.—CTD6 [34] + Milwaukee avg. from present study—(CTD7)	DR, P	Coal tar NIST SRM1597 (CTR2) [13]	DR
Creosote	Creosote-treated wood piling (CRE3) [13]	DR	Creosote product (CRE4) [2]	DR, P
	Creosote-treated railway ties (CRE2) [59]	DR, P		
Miscellaneous	Fuel-oil comb. particles (FOC1) [34]	P	Crude oil comb. (CRCB) [13]	DR
	No. 2 fuel oil comb. (FOC2) [13]	DR	Lubricating oil, re-refined (LUBR) [13]	DR
	Kerosene comb. (KERC) [13]	DR		

DR = diagnostic ratios; P = PAH profiles and principal components analysis and Chemical Mass Balance Model; avg = average; emis. = emissions; comb. = combustion.

[*a*]anthracene+chrysene), indeno[1,2,3-*cd*]pyrene/(indeno[1,2,3-*cd*]pyrene+benzo[*g,h,i*]perylene), and benzo[*b*]fluoranthene/benzo[*k*]fluoranthene. These ratios use compounds within a given molecular mass, which minimizes confounding factors such as weathering, volatility, and water solubility [13]. Ratios were not computed in cases of nondetections. Double-ratio plots and Euclidean distances between published source ratios (Table 1) and sample ratios were used to identify sources with ratios most similar to the samples.

PAH profiles

The PAH profiles of sources and streambed sediment samples were compared quantitatively for a subset of 12 PAHs (Supplemental Data, Tables S2 and S4). This 12-PAH subset enabled utilization of PAH source profiles from previous studies [7,14,34]. A mean profile of proportional PAH concentrations was computed for 33 streambed sediment samples; 6 streambed sediment samples (LIN-04, MIL-03, WIL-01, LMN-03, LYO-01, and KKR-03) were omitted because of nondetections, and the West Milwaukee Ditch sample (WMD-01) was analyzed separately because it had a profile that was very different from other samples. Creosote was analyzed separately from other sources because benzo[*e*]pyrene concentrations in creosote were not provided in the literature, and therefore the PAH profiles for the creosote sources included 11 instead of 12 compounds. A new source profile, CTD7, was created by averaging the 6 individual coal-tar–sealant parking lot dust profiles used in CTD6 [34] with the 2 Milwaukee parking lots assumed to be sealed with coal-tar sealant (rather than asphalt-based sealant) based on very high PAH concentrations in associated dust (mean of 22 800 mg/kg; PL-BANK, PL-DMV).

The similarity between PAH profiles of sources and streambed sediment samples was evaluated by using the chi-square statistic (χ^2), calculated as the square of the difference in proportional PAH concentrations divided by the mean of the 2 values, summed for the 12 PAHs [14]. A lower χ^2 indicates greater similarity between source and sample profiles.

Principal components analysis

Principal components analysis was performed using the same 12-compound PAH profiles discussed in the *PAH profiles* section (11-compound profiles for creosote sources; Supplemental Data, Table S4), with data standardized to have a mean of 0 and unit variance. Euclidean distances in *n*-dimensional space were computed between sources and samples in the space defined by the principal components that accounted for $\geq$10% of the variability. Sources with the shortest Euclidean distance to the samples were considered to be most similar to the samples. Graphs between all combinations of principal components 1 to 4 were also used to assess similarity among sources and samples. The principal component analysis computation was done using the prcomp function from the stats package in R [35].

Chemical Mass Balance receptor model

The USEPA CMB8.2 receptor model [36] was used to estimate the contributions of different PAH sources to streambed sediments. Although originally developed for atmospheric contaminants, the CMB model has been applied to sediment contaminants by numerous studies [7,14,37,38]. Modeling procedures developed in those studies were used in the present study. Twelve-compound PAH profiles were used for PAH sources and sediment samples (Supplemental Data, Table S4). Each model run attempted to fit numerous PAH source profiles to an individual sediment sample profile by using source elimination with up to 20 iterations [7]. Uncertainty was set at 40% for source profiles and at 20% for sediment sample profiles, with a default minimum source projection of 0.95 [7]. Samples with 1 or more nondetections in the 12-compound PAH profile were not included (LIN-04, MIL-03, WIL-01, LMN-03, LYO-01, and KKR-03). Model results were output as comma-separated value files for analysis in the R statistical computing software [35].

Two rounds of CMB model runs were done: the first used a wide array of PAH source profiles, and the second used a narrower set of PAH source profiles. In the first round, the model was run 75 times for each sample, using different combinations of sources (Supplemental Data, Table S5). Each run included 4 to 7 PAH sources; inclusion of more than 7 sources often resulted in failure to converge, likely because of collinearity between PAH sources [7]. One source profile from each of the following source categories was included in all runs: coal combustion, vehicle emissions, wood combustion, and either asphalt or coal-tar–sealant pavement dust. Numerous studies have found that coal-tar sealant is a major source of PAHs to streams [7,12,14,39,40]; excluding it from some models and instead including asphalt provided a negative control for coal-tar sealant. Additional PAH source profiles often included in model runs were motor oil, fuel oil combustion, and tire particles. Multiple PAH profiles were available in the literature for some sources, such as coal combustion, used motor oil, wood combustion, and coal-tar–sealant dust. In such cases the profile most similar to the streambed sediment profiles was used, as determined from the PAH profile comparisons discussed in the *PAH Profiles* section. The creosote-related sources (CRE2 and CRE4) were not included in the CMB model because PAH profile comparisons and principal components analysis both indicated little similarity between these sources and the Milwaukee streambed sediment samples, and because the 12-compound profile used in the CMB model was not available for the creosote sources.

The results of the first round of CMB model runs were filtered based on basic model performance measures. As described in Coulter [36], models were excluded from further consideration if R^2 values were less than 0.8, χ^2 values were greater than 2.0, or mass percentage (measured concentration/model-estimated concentration) was outside of 80% to 120%. The remaining models for each sample were ranked based on their R^2 and χ^2 values, and the ranks were used to identify the 10 best models for each sample. The 5 to 6 most frequently occurring sources within the 10 best models were used as the final source inputs for each sample in the second round of CMB model runs.

The second round of CMB model runs consisted of 4 scenarios for each sample: with and without phenanthrene in the PAH profiles, and with and without coal-tar–sealed pavement dust as a potential source. Models with and without phenanthrene were run because past studies have noted model overestimation of that compound because of its low molecular weight and volatility [14]. Running the model without coal-tar–sealed pavement dust provided a negative control to evaluate model performance without that source. The R^2, χ^2, mass percentage, and *T*-statistics of the final 4 models were used to identify the overall best model for each sample.

Table 2. Summary of polycyclic aromatic hydrocarbons (PAHs) and toxicity quotients for individual samples

Site abbreviation[a]	TOC (%)	ΣPAH_{16} (mg/kg)	Parent:alkyl ratio	HMW:LMW ratio	PECQ	TECQ	ΣESBTU
Streambed sediment samples							
BUT-01	4.3	73.9	3.1	4.9	3.2	45.9	2.7
DOU-01	10.0	120	2.3	4.7	5.3	74.6	2.0
EDG-01	5.8	40.7	2.1	5.5	1.8	25.3	1.2
HON-01	1.3	33.7	2.5	4.3	1.5	21.0	4.3
HON-02	3.9	93.0	2.5	4.1	4.1	57.8	4.0
KKR-02	3.7	125	2.5	2.3	5.5	77.5	6.0
KKR-03	0.3	1.4	0.0	4.0	0.1	0.9	1.2
LIN-01	5.6	57.0	2.0	4.2	2.5	35.4	1.7
LIN-02	2.1	83.6	2.4	3.9	3.7	51.9	6.7
LIN-03	5.6	208	4.2	4.0	9.1	129	5.9
LIN-04	0.7	2.1	0.2	2.6	0.1	1.3	0.7
LLY-02	3.0	4.6	2.3	4.2	0.2	2.8	0.3
LMN-01	2.6	24.3	2.2	4.8	1.1	15.1	1.6
LMN-02	3.5	13.5	3.2	6.8	0.6	8.4	0.6
LMN-03	5.4	0.6	2.5	2.3	0.0	0.4	0.0
LYO-01	1.4	6.0	0.0	3.7	0.3	3.7	1.3
MEN-01	2.5	32.9	2.6	3.8	1.4	20.5	2.2
MEN-02	1.0	41.0	2.9	4.7	1.8	25.4	6.6
MEN-03	7.3	57.1	2.3	5.4	2.5	35.5	1.3
MEN-04	2.3	1.5	2.4	2.8	0.1	0.9	0.1
MEN-05	3.9	36.6	2.7	4.6	1.6	22.7	1.5
MIL-01	6.8	25.6	2.2	4.3	1.1	15.9	0.6
MIL-02	4.4	54.0	1.5	2.9	2.4	33.6	2.4
MIL-03	1.7	3.5	0.0	3.1	0.2	2.1	0.6
MIL-04	3.9	31.1	2.5	4.9	1.4	19.3	1.3
NOR-01	3.3	128	2.9	5.0	5.6	79.4	6.2
NOY-01	3.7	35.4	2.3	3.2	1.6	22.0	1.7
ROO-01	1.8	20.5	2.8	5.3	0.9	12.8	1.8
ROO-03	3.0	131	3.1	3.5	5.8	81.5	7.2
ROO-04	1.8	12.9	3.0	3.9	0.6	8.0	1.2
ROO-06	6.1	84.2	2.4	5.3	3.7	52.3	2.2
ROO-07	0.7	31.2	2.9	4.5	1.4	19.4	7.0
SCH-01	1.6	13.2	2.3	4.7	0.6	8.2	1.4
UND-02	2.5	5.7	3.7	5.2	0.3	3.6	0.4
UND-03	2.4	169	3.0	3.5	7.4	105	11.5
UND-04	2.8	104	2.6	3.7	4.5	64.4	6.2
WIL-01	5.4	1.9	2.7	3.0	0.1	1.2	0.1
WMD-01	1.1	119	6.7	6.8	5.2	74.2	17.1
WPC-01	4.8	132	2.5	3.8	5.8	82.1	4.6
WPC-02	4.4	44.2	2.5	4.1	1.9	27.4	1.7
Parking lot dust samples							
PL-AZ	3.3	16.5	2.5	5.6	0.7	10.2	0.8
PL-BSM	1.5	5.3	1.7	3.8	0.2	3.3	0.6
PL-SRM	2.8	2.7	1.1	3.5	0.1	1.6	0.2
PL-BANK	7.0	24,907	6.1	5.7	1,092	15,471	531
PL-DMV	3.5	20,621	4.5	3.0	905	12,809	929
PL-MLHS	7.1	14.2	2.6	5.8	0.6	8.8	0.3

[a]See Supplemental Data, Table S1 for definitions of site abbreviations.
TOC = total organic content; ΣPAH_{16} = sum concentration of US Environmental Protection Agency 16 priority pollutant PAH compounds; HMW = high molecular weight; LMW = low molecular weight; PECQ = consensus-based probable effect concentration quotient; TECQ = consensus-based threshold effect concentration quotient; ΣESBTU = sum equilibrium partitioning sediment benchmark toxicity unit.

Mass fractions

Mass fraction analysis was used to evaluate how much of a PAH source material, in mass percentage, would be necessary to achieve the PAH concentrations measured in Milwaukee streambed sediment samples. The ΣPAH_{16} concentrations in samples were divided by mean PAH concentrations of potential sources gathered from the literature. For each potential source of PAHs, this analysis provided a hypothetical mass fraction of source material in each sediment sample, assuming negligible contributions from other sources. This method has been used as a tool to eliminate potential PAH sources as the primary source to environmental samples because of unlikely or even impossible mass fractions of source material required to achieve environmental concentrations [16].

RESULTS

Observed concentrations

Total PAH_{16} concentrations in streambed sediment ranged from 0.6 mg/kg to 208 mg/kg, with a mean and median of 55.1 mg/kg and 36.0 mg/kg, respectively (Table 2; Supplemental Data, Table S6; see also the *Data availability* statement). The dust samples from concrete and unsealed asphalt parking lots (PL-AZ, PL-BSM, and PL-SRM) had ΣPAH_{16} concentrations of 2.7 mg/kg to 16.5 mg/kg, similar to or lower than concentrations measured in most streambed sediment samples, eliminating dust from these types of surfaces as primary PAH sources to the streambed sediment. The concentrations in dust vacuumed from 2 of the 3 sealed asphalt parking lots (PL-BANK, 24 908 mg/kg; PL-DMV, 20 622 mg/kg) were

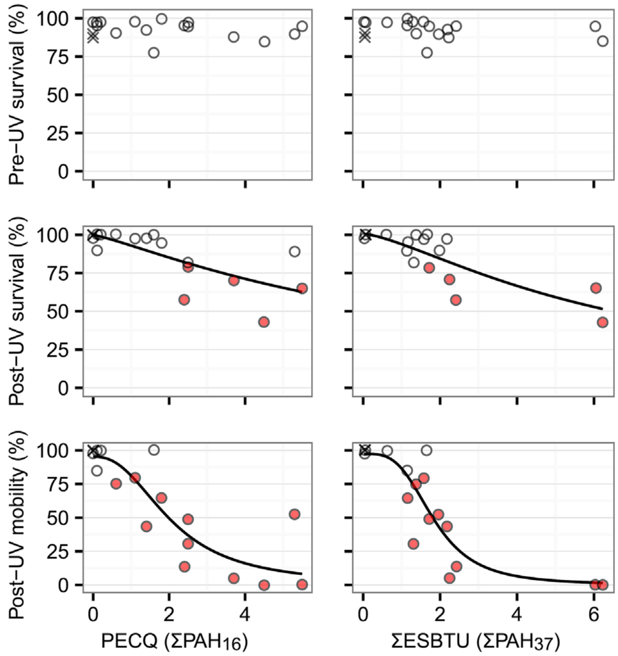

Figure 2. Relations between computed sediment-quality quotients (probable effect concentration quotients [PECQ] and sum equilibrium partitioning sediment benchmark toxicity units [ΣESBTU]) and mean responses of *Hyalella azteca* in laboratory exposures to streambed sediment samples. Fitted lines are from 3-parameter log-logistic regression. X = controls; circles = environmental samples; red-filled circles = samples with statistically significant reductions relative to control; UV = ultraviolet light; ΣPAH_n = sum of n polycyclic aromatic hydrocarbon compounds.

3 orders of magnitude higher than those from the concrete and unsealed lots and comparable to concentrations previously reported for coal-tar–based pavement sealant dust [41]. Dust vacuumed from the third sealed asphalt parking lot, PL-MLHS, had a ΣPAH_{16} concentration of 14.7 mg/kg, in the range of concentrations previously reported for dust swept from asphalt-seal–coated pavement [41].

Toxicity to aquatic organisms

A PECQ benchmark value of 1.0 was exceeded in 68% of the streambed sediment samples, and a ΣESBTU benchmark value of 1.0 was exceeded in 78% of streambed sediment samples (Table 2). The highest PECQ was 9.1, occurring at LIN-03 (Lincoln Creek at 76th Street), and the highest ΣESBTU was 17.1, occurring at WMD-01 (West Milwaukee Ditch). The TECQs exceeded 1.0 in 37 of 40 streambed sediment samples.

Prior to UV exposure, *H. azteca* and *C. dilutus* survival rates were not significantly different in samples than in controls in the 16 streambed sediment samples included in laboratory toxicity tests (Supplemental Data, Table S7). Significant reductions, relative to control, in dry weight and in biomass of amphipods or midges were measured in 3 samples (19%). Following UV exposure of *H. azteca*, significant reductions in survival (relative to control) were observed in 5 of 16 samples (31%), and significant reductions in mobility (relative to control) were observed in 11 of 16 samples (69%; Figure 2). Significant immobility of *H. azteca* was observed in 85% and 91% of samples that had ΣESBTU and PECQ values greater than 1.0, respectively.

Identification of PAH sources

Land-use analysis. Of 5 primary urban land-use categories (residential, roads and streets, parking, commercial, and industrial), only 2 were significantly related to ΣPAH_{16} concentrations: parking lot coverage in the drainage area and commercial land use (Figure 3). Parking lot land use was most strongly correlated with ΣPAH_{16} concentrations, with a Spearman's rank correlation coefficient of 0.75 (Figure 3C). Commercial land use, which includes areas such as stores, malls, restaurants, and businesses, but does not include adjacent parking areas, had a Spearman's rank correlation coefficient of 0.65. General urban land use (the combination of the 5 primary

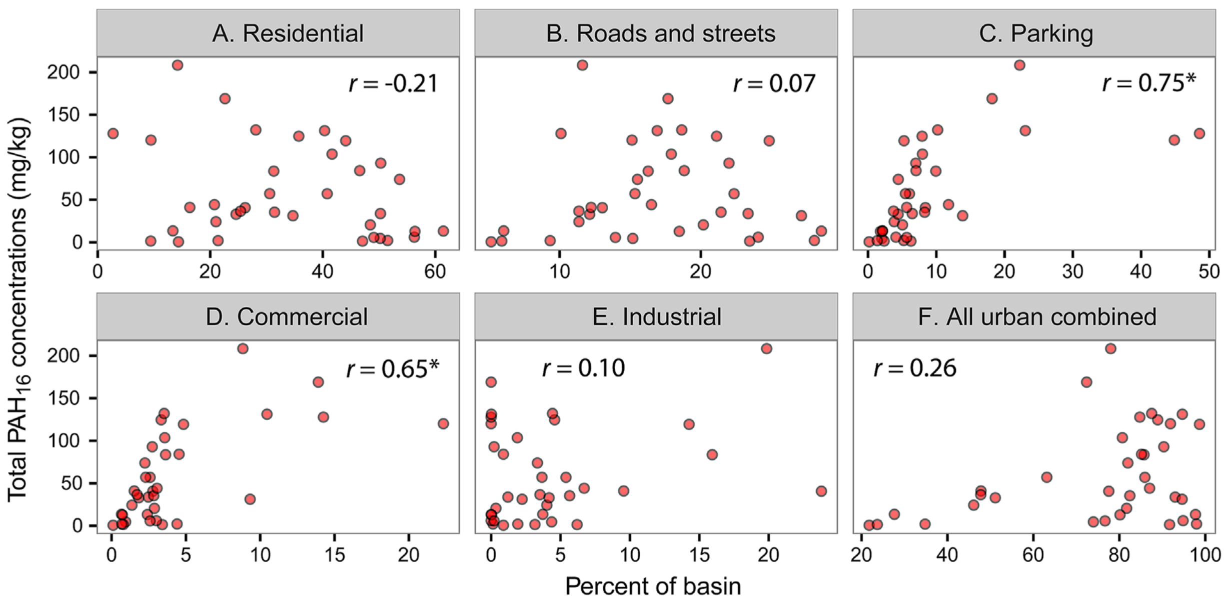

Figure 3. Relations between streambed sediment total PAH_{16} concentrations and the percentage of each basin in different urban-related land uses. Land uses in (**F**) are the sum of (**A–E**). An asterisk represents significant differences at $p < 0.05$. r = Spearman correlation coefficient; PAH_{16} = 16 polycyclic aromatic hydrocarbon compounds.

urban land-use categories; Figure 3F) was not significantly related to ΣPAH_{16} concentrations.

Parent/alkyl and high molecular weight/low molecular weight PAH compounds

Parent PAH compounds were dominant over alkylated PAH compounds in Milwaukee streambed sediment samples, indicating a pyrogenic rather than petrogenic PAH source [2]. The median ratio of parent:alkylated compounds in the 40 streambed sediment samples was 2.5 (Supplemental Data, Figure S2). The median ratio of high molecular weight:low molecular weight compounds was 4.2, also indicating a dominantly pyrogenic source of PAHs [7].

Diagnostic ratios

The PAH compound ratios of streambed sediment samples at most sites were very similar regardless of the PAH concentrations of the samples, suggesting a common PAH source (Figure 4). Of all sources considered, coal-tar–sealed pavement dust ratios (CTD6, CTD7) were most similar to those of the streambed sediment samples on the basis of the shortest mean Euclidean distances between ratios of sources and samples (Figure 4; Supplemental Data, Table S8). Other sources with ratios similar to streambed sediment samples in at least 1 of the double-ratio plots but not all double-ratio plots included creosote product (CRE4) and creosote-treated wood pilings (CRE2), coal tar SRM1597 (CTR2), hard coal briquette combustion (CCB4), bituminous coal combustion (CCB3), grass combustion (GRAS), kerosene (KERO), wood soot (WDST), and urban air (URBN).

The 6 Milwaukee parking lot dust samples clustered with or near the stream samples for each of the diagnostic ratio evaluations (Figure 4). The parking lot samples also closely matched those of coal-tar–sealant dust, regardless of the parking lot composition or sealed status (concrete, unsealed asphalt, or sealed asphalt).

The median BbF/BkF ratio of streambed sediment samples (not plotted because of limited source information) was 2.54 (range, 2.21–3.07). The parking lot samples had similar ratios, with a median of 2.56 (range, 2.41–2.71). The median ratios were virtually identical to the BbF/BkF ratio of 2.53 reported for weathered coal-tar–sealant scrapings [42]. Reported BbF/BkF ratios for NIST SRM diesel particulate matter and urban dust were 2.94 and 3.43, respectively [43,44].

The median FluA/Pyr ratio of streambed sediment samples (not plotted) was 1.35 (range, 0.13–1.58), similar to the mean reported for coal-tar–sealant pavement dust from 6 US cities (1.34 [34]) and also to coal-tar product (1.29 [45]). Other sources with a similar ratio included iron/steel plant flue gas (1.43), wood-burning emissions (1.26), diesel engine soot (1.26), and highway dust (1.40) [2]. Sources with a dissimilar ratio include urban background (0.9 ± 0.2), urban runoff (0.23–1.07), creosote (1.52–1.70), creosote-contaminated sediment (1.59), and asphalt (<0.11) [2,46].

PAH profiles

The PAH profiles of the 33 streambed sediment samples were very similar to one another and most closely matched the source profile of coal-tar–sealed pavement dust (Figure 5; Supplemental Data, Figures S3 and S4). The χ^2 statistic between the mean profile of the 33 streambed sediment samples and that of the PAH source CTD7 was 0.008, 1 to 2 orders of magnitude lower than with other PAH sources (Supplemental Data, Table S9). Sample WMD-01, analyzed separately from other

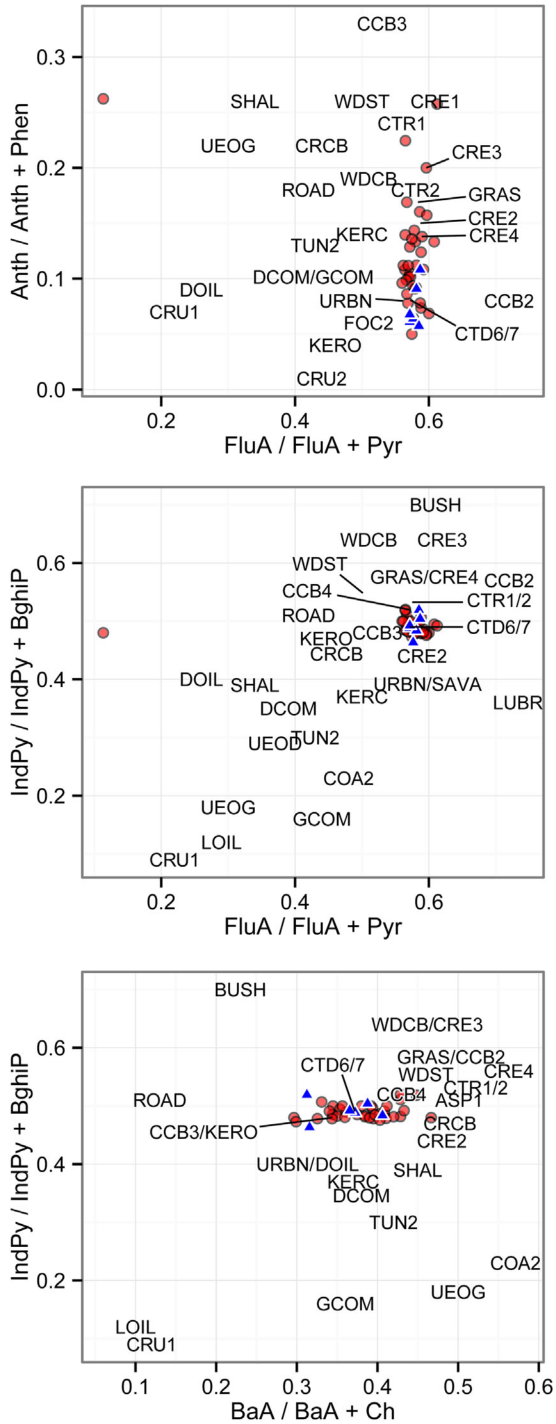

Figure 4. Double-ratio plots of diagnostic compound ratios of polycyclic aromatic hydrocarbon (PAH) sources (abbreviations given in Table 1) and Milwaukee (WI, USA) streambed sediment (circles) and parking lot dust samples (triangles). Anth = anthracene; Phen = phenanthrene; FluA = fluoranthene; Pyr = pyrene; IndPy = indeno[1,2,3-*cd*]pyrene; BghiP = benzo[*g,h,i*]perylene; BaA = benz[*a*]anthracene; Ch = chrysene.

streambed sediment samples because of its different profile, did not closely match any of the sources (Supplemental Data, Figures S5 and S6).

Principal components analysis

Two separate principal components analyses were performed, 1 using the 12-compound PAH profiles and all noncreosote sources and the other using the 11-compound

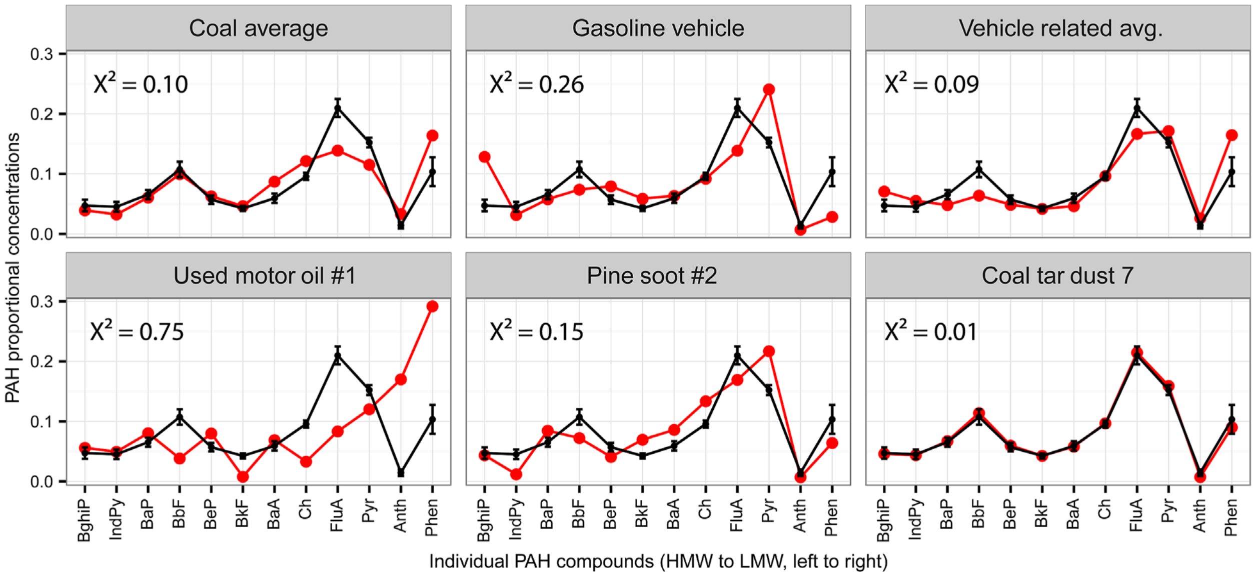

Figure 5. Comparison of polycyclic aromatic hydrocarbon (PAH) profiles for 6 sources (red) to the mean (± standard deviation) profile for 33 Milwaukee (WI, USA) streambed sediment samples (black). Compound abbreviations are defined in Table 1. X^2 = chi-square statistic.

PAH profiles and all sources, including creosote. In the 12-compound analysis, principal components 1 to 4 each explained more than 10% of the variance for a cumulative 79% of the variance in the overall dataset (Supplemental Data, Figure S7). In the 11-compound analysis, principal components 1 to 4 each explained more than 10% of the variance for a cumulative 81% of the variance (Supplemental Data, Figure S8). Using 4 components from each of the 12- and 11-compound principal component analysis results, Euclidean distances between sources and the streambed sediment samples, computed for all paired combinations of principal components, consistently identified coal-tar–sealant dust as the source with PAH profiles most similar to streambed sediment samples (Figure 6; Supplemental Data, Figure S9). In addition, pairwise graphs of all combinations of components 1 to 4 for these principal component analyses indicated that the PAH profile of coal-tar–sealant dust was similar to most samples (Supplemental Data, Figures S7 and S8). Other sources plotting near-streambed sediment samples in some, but not all, principal component combination graphs were pine combustion #1, coal combustion average, and vehicle average. Sources most distant from streambed sediment samples were coke oven emissions, used motor oil (numbers 1 and 2), fuel oil combustion, tire particles, oak combustion, and creosote.

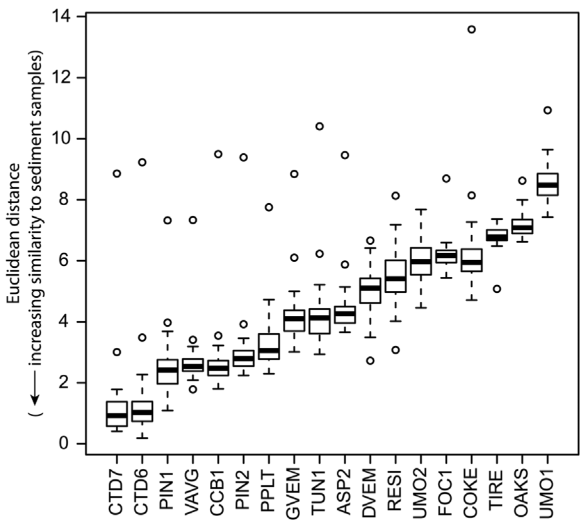

Figure 6. Euclidean distances between sources (excluding creosote) and samples for principal components analysis components 1 through 4 using 12-compound polycyclic aromatic hydrocarbon (PAH) profiles. Boxes = 25th to 75th percentiles; dark line = median; whiskers = 1.5 × the interquartile range (IQR); circles = values outside 1.5 × the IQR; CTD7 = coal-tar–sealed pavement dust, 7-city average; CTD6 = coal-tar–sealed pavement dust, 6-city average; PIN1 = pine wood soot particles #1; VAVG = vehicle/traffic average; CCB1 = coal average; PIN2 = pine wood soot particles #1; PPLT = power plant emissions; GVEM = gasoline vehicle particulate emissions; TUN1 = traffic tunnel air; ASP2 = asphalt; DVEM = diesel vehicle particulate emissions; RESI = residential heating; UMO2 = used motor oil #2; FOC1 = fuel-oil combustion particles; COKE = coke oven emissions; TIRE = tire particles; OAKS = oak wood soot particles; UMO1 = used motor oil #1.

Chemical Mass Balance receptor model

For each streambed sediment sample, the CMB model was run 79 times to converge on the 3 to 5 most likely PAH sources. Six samples were omitted because of nondetections, and WMD-01 was omitted because all models for that sample failed to meet the basic model performance criteria described in the CMB Manual ($R^2 > 0.8$, $\chi^2 < 2.0$, mass percentage between 80% and 120% [36]), indicating that the primary source of PAHs in WMD-01 was not available in the model.

The R^2 values of the final models for each of the remaining 33 samples were 0.96 to 1.00 (median, 1.00), χ^2 values were 0.01 to 0.42 (median, 0.05), and percentage mass values were 96.3 to 103.6 (median, 100.4; Supplemental Data, Table S10). Based on the final models, coal-tar–sealant pavement dust was an important PAH source (T-statistic > 2.0) to all 33 samples, and was the primary PAH source to 32 samples (Figure 7). The model-estimated contribution of coal-tar–sealant pavement dust ranged from 41% to 94% (mean, 77%; median, 78%) of the total PAHs in each sample. Contributions from other sources often did not meet the basic model performance criteria (T-statistic < 2.0), lending support to the inclusion of only 4 to 7 sources in each model run.

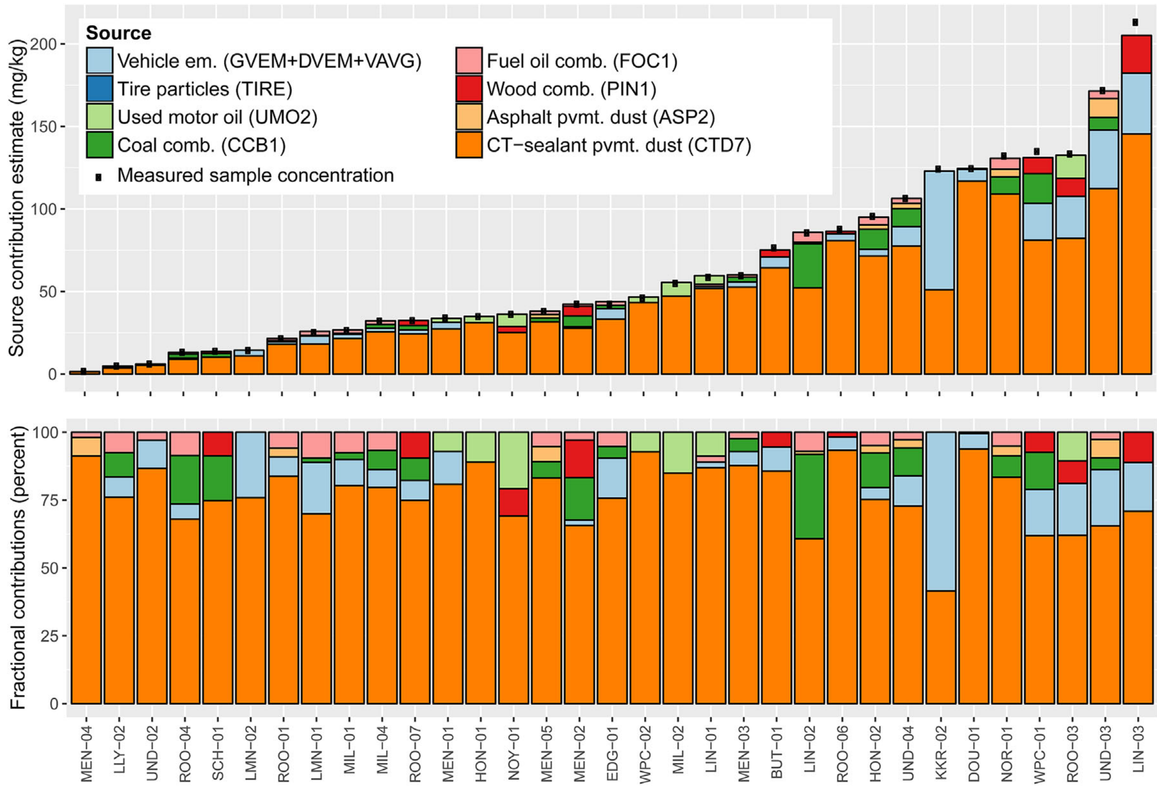

Figure 7. Source contributions of polycyclic aromatic hydrocarbons (PAHs) to Milwaukee (WI, USA) streambed sediment samples estimated by using the US Environmental Protection Agency Chemical Mass Balance Model. em. = emissions; comb. = combustion; pvmt. = pavement; CT = coal-tar; source abbreviations are in Table 1.

Those models in the second round that did not include coal-tar–sealant dust generally had poorer model fit. Including coal-tar–sealant pavement dust improved the model R^2 by 0.06 (mean) and the χ^2 by 0.67 (mean; Supplemental Data, Table S11). Mass percentage values averaged 100.2% in models that included coal-tar–sealant pavement dust, and 96.6% in models excluding it, indicating that coal-tar–sealant pavement dust was an important source.

Mass fractions

Many PAH sources identified in Table 1 could not have been the primary source of PAHs to Milwaukee streambed sediment

Table 3. Mass fraction of source material in sediment samples necessary to achieve measured polycyclic aromatic hydrocarbon (PAH) concentrations, assuming contributions from no other sources (based on mean concentrations of each source from the literature)

	ΣPAH_{16} concentrations (mg/kg)		Mass fraction (%)	
PAH sources (*n*) [reference]	Mean	Maximum	Median of samples	Maximum of samples
Particulates				
Creosote-treated wood (7) [59,60]	63 365	97 181	0.06	0.33
CT-sealant scrapings (7) [42]	15 843	25 800	0.23	1.31
CT-sealed pavement dust (11) [41]	4817	11 300	0.75	4.32
Gasoline exhaust/soot (2) [61]	992	1465	3.63	21.0
Diesel exhaust/soot (7) [61]	115	671	31.2	> 100
Tire particles (6) [61,62]	106	226	34.0	> 100
Road dust (1) [62]	58.7	58.7	61.3	> 100
Traffic tunnel dust (5) [63]	22.6	25.0	> 100	> 100
Unsealed asphalt pavement dust (7) [41]	17.2	48.7	> 100	> 100
Brake lining particles (1) [62]	16.2	16.2	> 100	> 100
Wood combustion (4) [64,65]	14.1	29.7	> 100	> 100
Concrete parking lot dust (2) [41]	11.4	15.1	> 100	> 100
Asphalt (12) [16,61]	11.1	28.0	> 100	> 100
Asphalt-sealed pavement dust (3) [41]	8.50	10.9	> 100	> 100
Liquids				
CT sealant product (1) [42]	30 900	30 900	0.12	0.67
Motor oil, used (9) [61,66]	610	1295	5.90	34.1
Motor oil, unused (1) [66]	2.6	2.6	> 100	> 100

ΣPAH_{16} = sum concentration of US Environmental Protection Agency 16 priority pollutant PAH compounds; *n* = number of samples; CT = coal tar.

samples because they have PAH concentrations lower than those in streambed sediment (Table 3), even before being diluted by the silt, sand, and organic material that make up the bulk of streambed sediment. For example, the median streambed sediment sample concentration of 36 mg/kg (ΣPAH_{16}) was greater than the typical concentration of traffic tunnel dust, unsealed asphalt pavement dust, brake lining particles, wood combustion, concrete parking lot dust, asphalt, and asphalt-sealed pavement dust, eliminating these as likely primary sources. In fact, for most PAH sources, an unlikely mass fraction of source material (>5%) would have been required to achieve the streambed sediment sample PAH concentrations measured in the present study. Only those PAH sources with the highest concentrations—those related to creosote and coal-tar sealant—could reasonably have achieved the concentrations observed in most streambed sediment samples at realistic mass fractions (<5% [16]).

DISCUSSION

The ΣPAH_{16} concentrations in streambed sediment measured in the present study (1.6–208 mg/kg; median, 36.0 mg/kg), which are comparable to or higher than concentrations in sediments from other urban areas in the United States [7,12,39,40,47], likely adversely affect ecosystem health. The PAH-specific sediment quality guidelines (PECQs and ΣESBTUs) and laboratory toxicity tests indicate likely toxicity of these streambed sediments to benthic organisms at as many as 78% of sampled streams. Other studies support these findings. A laboratory study of frogs (*Xenopus laevis*) found significantly stunted growth and slower development after exposure to coal-tar–sealant spiked sediment with a ΣPAH_{16} concentration of 30 mg/kg and complete mortality at a ΣPAH_{16} concentration of 300 mg/kg [48]. Another study reported significant effects on aquatic community health, including species abundance and richness, at stream sites with higher PAH concentrations (ΣPAH_{16} 0.75–32 mg/kg) compared with upstream locations with lower PAH concentrations (ΣPAH_{16} 0.04–3.9 mg/kg) [39].

Laboratory toxicity tests on *H. azteca* showed no adverse effects prior to UV exposure, despite PAH concentrations in many samples well above sediment quality guidelines. However, after the 4-h UV exposure, *H. azteca* exhibited significantly decreased mobility and survival with increasing PAH concentrations, consistent with sediment quality guideline–based estimates. The UV-induced toxicity (phototoxicity) is important because UV transmission to the benthos is likely at many of the sampled streams, characterized by clear, shallow water (<50-cm depth) and partial or no canopy cover [49]. The PAHs are among the most potent and most commonly occurring phototoxic compounds in urban areas [50,51], and PAH-related phototoxicity has been reported by a number of studies [26,52–54], with UV radiation increasing toxicity by up to several orders of magnitude [26,54]. The occurrence of toxicity only after UV exposure in the present study is a strong indicator that PAHs were the cause of the toxicity, rather than other contaminants potentially present in the sediment.

The source identification methods used in the present study have important limitations and uncertainties. Some of these include uncertainties in PAH compound concentrations for both the PAH sources (from the literature) and the streambed sediment samples, varying levels of PAH data quality in the literature, inability of ratios and profiles to completely capture the variability in PAH sources, the potential for weathering to affect PAH profiles in sediment samples, and potential misinterpretation of results if an important PAH source is not included in the analysis. The use of a multiple-lines-of-evidence approach mitigates the uncertainties of individual methods and strengthens the overlapping conclusions [10,11]. The land-use analysis is the least influenced by these uncertainties because it relies only on total PAH concentrations and watershed attributes.

The source identification methods used in the present study consistently indicated that coal-tar–based pavement sealant was likely the primary source of PAHs to the majority of sampled streambed sediments. The dominance of high molecular weight over low molecular weight compounds and the dominance of parent over alkylated compounds both indicated a pyrogenic rather than petrogenic source (Supplemental Data, Figure S1). Therefore, uncombusted petroleum products—including gasoline, diesel, home heating oils, and engine oils—were not likely to be primary sources of PAHs to the sediments sampled. Mass fraction analysis demonstrated that PAH concentrations of most of the pyrogenic source candidates are too low for these sources to have been primary PAH contributors to the Milwaukee sediments (Table 3) because these sources would have to make up an unrealistic proportion (e.g., >5%) of the mass of the sampled streambed sediment to achieve the measured PAH concentrations.

Only 2 sources have PAH concentrations sufficiently high to achieve the measured streambed sediment concentrations with realistic mass fractions: creosote and coal-tar–sealed pavement dust; however, diagnostic ratios, PAH profiles, and principal components analysis demonstrated that creosote and creosote-treated wood profiles were poorly correlated with those of the Milwaukee samples. Therefore, despite creosote's high PAH concentrations, and the presence of railways and other creosote-treated wood in many of the sampled watersheds, creosote is unlikely to have been the primary source to streambed sediments in the present study. A study of the migration of PAHs from creosote-treated railway ties into adjacent wetlands found that after the first year of weathering there was no significant loss of PAHs from the ties, suggesting that decades-old, weathered railway ties and other creosote-treated wood likely contribute insignificant amounts of PAHs to Milwaukee-area streams [55]. Even in Milwaukee's Little Menomonee River, a stream with Superfund status for historic (1921–1976) creosote contamination, a study conducted in 2008 (after cleanup of much of the stream) estimated that creosote contributed only 19% of the total PAHs in shallow streambed sediments (0–6 inches [56]).

The conclusion that coal-tar–based sealcoat is a primary PAH source to stream sediment is further supported by the significant relation between PAH concentrations and the percentage of parking area in the drainage basin ($r = 0.75$; Figure 3) and lack of a significant relation with the percentage of road and street area in the drainage basin ($r = 0.07$). Parking areas and roads and streets have many similarities: they are impervious surfaces made of asphalt or concrete, they accumulate exhaust, tire, and brake particles, as well as leaking motor oil from cars and trucks, and they receive atmospheric deposition of PAHs. A key difference between the 2 land-use categories, however, is that parking areas, if made of asphalt, commonly are treated with pavement sealants, whereas roads and streets typically are not sealed. Coal-tar–based pavement sealants, the dominant formulation used in this part of the United States (i.e., east of the Rocky Mountains) [57], contain high PAH concentrations (Table 3). The dried sealant can wear off, and the resulting particles can be transported by storm water runoff from parking lots [5] and accumulate in downstream sediments, increasing sediment PAH concentrations by an order of magnitude or more [4,40]. The significant relation between PAH concentrations and commercial land use ($r = 0.65$) likely resulted from the fact that commercial land use requires parking areas, and these 2 land uses are significantly correlated ($r = 0.85$). The poor relation between PAH concentrations and all urban land uses combined ($r = 0.26$) indicates that urban land use in and of itself was not a primary factor controlling PAH concentrations. A land-use study in Springfield (MO, USA) reported similar findings, with sediment PAH concentrations strongly correlated with the percentage of sealed parking lot area within the upstream drainage area of the sampling site, but poorly correlated with urban land use in general [12].

The presence of PAHs in urban areas is often attributed to urban background, a collective term for typical urban sources such as atmospheric deposition of coal and petroleum combustion particles. Stout et al. [46] provided a general rule-of-thumb that ΣPAH_{16} sediment concentrations of approximately 20 mg/kg or less are likely attributable to urban background, but higher concentrations indicate additional point-source contributions. Of the 40 streambed sediment samples in the present study, 70% had PAH concentrations that exceeded 20 mg/kg, and 48% had a PAH concentration more than twice that, indicating that urban background alone cannot account for a large portion of the PAHs. The poor relation between PAH concentrations and urban land use supports this conclusion (Figure 3).

The near-ubiquity of the coal-tar signature in streambed sediment and parking lot dust samples collected for the present study likely results from the extremely high PAH concentration of coal-tar pavement sealant relative to concentrations in other urban sources. Coal tar has such a high concentration of PAHs that even a very small quantity is likely to overwhelm the signature of other PAH sources, and isomer ratios reflect only the coal tar [16]. Because of the coal-tar–sealant strength, and because sealant particles are mobile, storm water runoff, wind, and tires disseminate the particles—and their PAH signature—throughout the urban landscape [16,57]. This can even cause dust from unsealed parking lots to have a coal-tar–sealant signature, as was evidenced in the present study. Similarly, a petrographic analysis of dust from unsealed pavement in Fort Worth (TX, USA) reported that 92% of the PAHs in the dust were from coal-tar pitch [58].

In conclusion, multiple lines of evidence indicate that coal-tar–based pavement sealant was the primary source of PAHs to the majority of streambed sediment samples collected in the present study. Each diagnostic method identified a different suite of potential PAH sources, but only coal-tar–based pavement sealant was indicated by all methods. The CMB model estimated, on average, that 77% of total PAHs to streambed sediment samples came from coal-tar–based pavement sealant dust, similar to findings in Springfield (MO, USA; >80% [12]) and Minneapolis (MN, USA; 67% [7]). Removing the PAH contribution from coal-tar–based pavement sealant dust to Milwaukee-area streams would reduce the median PECQ from 1.8 to 0.3 and lower the percentage of sampled sites exceeding the PEC from 68% to 20%. Toxicity tests in the present study and in others [19] indicate that such a large reduction in PECQs would significantly improve stream health.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.3694.

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Disclaimer—Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the US Government.

Data Availability—Data are provided in the Supplemental Data and are available online at https://doi.org/10.5066/F7P55KJN.

REFERENCES

1. Van Metre PC, Mahler BJ, Furlong ET. 2000. Urban sprawl leaves its PAH signature. *Environ Sci Technol* 34:4064–4070.
2. Neff JM, Stout SA, Gunster DG. 2005. Ecological risk assessment of polycyclic aromatic hydrocarbons in sediments: Identifying sources and ecological hazard. *Integr Environ Assess Manag* 1:22–33.
3. Pietara J, O'Reilly K, Boehm P. 2010. A Review of PAHs | Articles | Stormwater. *Stormwater* [cited 2014 December 31]. Available from: http://www.stormh20.com/SW/Articles/A_Review_of_PAHs_11549.aspx
4. Mahler BJ, Van Metre PC, Bashara TJ, Wilson JT, Johns DA. 2005. Parking lot sealcoat: An unrecognized source of urban polycyclic aromatic hydrocarbons. *Environ Sci Technol* 39:5560–5566.
5. Selbig WR. 2009. Concentrations of polycyclic aromatic hydrocarbons (PAHs) in Urban stormwater, Madison, Wisconsin, 2005-08. US Geological Survey. [cited 2014 December 31]. Available from: http://pubs.usgs.gov/of/2009/1077/.
6. Eisler R. 1987. Polycyclic aromatic hydrocarbon hazards to fish, wildlife and invertebrates: A synoptic review. U.S. Department of the Interior, Fish and Wildlife Service, Laurel, MD. [cited 2016 March 23]. Available from: http://pubs.er.usgs.gov/publication/5200072
7. Crane JL. 2014. Source apportionment and distribution of polycyclic aromatic hydrocarbons, risk considerations, and management implications for urban stormwater pond sediments in Minnesota, USA. *Arch Environ Contam Toxicol* 66:176–200.
8. US Environmental Protection Agency. 2002. G*reat Lakes Legacy Act*. EPA R 05. [cited 2016 August 19]. Available from: https://www.epa.gov/great-lakes-legacy-act
9. Baldwin AK, Corsi SR, Richards KD, Geis SW, Magruder C. 2013. Organic waste compounds in streams: Occurrence and aquatic toxicity in different stream compartments, flow regimes, and land uses in southeast Wisconsin, 2006–9. US Geological Survey. [cited 2015 January 2]. Available from: http://pubs.usgs.gov/sir/2013/5104/.
10. Larsen RK, Baker JE. 2003. Source apportionment of polycyclic aromatic hydrocarbons in the urban atmosphere: A comparison of three methods. *Environ Sci Technol* 37:1873–1881.
11. O'Reilly KT, Pietari J, Boehm PD. 2014. Parsing pyrogenic polycyclic aromatic hydrocarbons: Forensic chemistry, receptor models, and source control policy. *Integr Environ Assess Manag* 10:279–285.
12. Pavlowsky RT. 2013. Coal-tar pavement sealant use and polycyclic aromatic hydrocarbon contamination in urban stream sediments. *Phys Geogr* 34:392–415.
13. Yunker MB, Macdonald RW, Vingarzan R, Mitchell RH, Goyette D, Sylvestre S. 2002. PAHs in the Fraser River basin: A critical appraisal of PAH ratios as indicators of PAH source and composition. *Org Geochem* 33:489–515.
14. Van Metre PC, Mahler BJ. 2010. Contribution of PAHs from coal-tar pavement sealcoat and other sources to 40 U.S. lakes. *Sci Total Environ* 409:334–344.
15. Demott RP, Gauthier TD, Wiersema JM, Crenson G. 2010. Polycyclic aromatic hydrocarbons (PAHs) in Austin sediments after a ban on pavement sealers. *Environ Forensics*. 11:372–382.
16. Ahrens MJ, Depree CV. 2010. A source mixing model to apportion PAHs from coal tar and asphalt binders in street pavements and urban aquatic sediments. *Chemosphere*. 81:1526–1535.
17. Geib WJ, Dunnewald TJ. Wisconsin Geological & Natural History Survey soil map: Wisconsin Milwaukee County sheet (B056A-map01). [cited 2016 August 19]. Available from: https://wgnhs.uwex.edu/pubs/b056amap01/.
18. Zaugg SD, Burkhardt MR, Burbank TL, Olson MC, Iverson JL, Schroeder MP. 2006. Determination of semivolatile organic compounds

and polycyclic aromatic hydrocarbons in solids by gas chromatography/mass spectrometry. In *US Geological Survey Technical Methods*, Book 5, Chapter B3. US Geological Survey, Reston, VA, USA, p 44.
19. Ingersoll CG, MacDonald DD, Wang N, Crane JL, Field LJ, Haverland PS, Kemble NE, Lindskoog RA, Severn C, Smorong DE. 2001. Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines. *Arch Environ Contam Toxicol* 41:8–21.
20. Kemble NE, Hardesty DK, Ingersoll CG, Kunz JL, Sibley PK, Calhoun DL, Gilliom RJ, Kuivila KM, Nowell LH, Moran PW. 2013. Contaminants in stream sediments from seven United States metropolitan areas: Part II-sediment toxicity to the amphipod *Hyalella azteca* and the midge *Chironomus dilutus*. *Arch Environ Contam Toxicol* 64:52–64.
21. US Environmental Protection Agency. 2003. Procedures for the derivation of equilibrium partitioning sediment benchmarks (ESBs) for the protection of benthic organisms: PAH mixtures. EPA 600/R-02/13. Washington, DC.
22. Besser JM, Brumbaugh WG, Ingersoll CG, Ivey CD, Kunz JL, Kemble NE, Schlekat CE, Garman ER. 2013. Chronic toxicity of nickel-spiked freshwater sediments: Variation in toxicity among eight invertebrate taxa and eight sediments. *Environ Toxicol Chem* 32:2495–2506.
23. Besser JM, Ingersoll CG, Brumbaugh WG, Kemble NE, May TW, Wang N, Macdonald DD, Roberts AD. 2015. Toxicity of sediments from lead-zinc mining areas to juvenile freshwater mussels (*Lampsilis siliquoidea*) compared to standard test organisms. *Environ Toxicol Chem* 34:626–639.
24. Ingersoll CG, Kunz JL, Hughes JP, Wang N, Ireland DS, Mount DR, Hockett JR, Valenti TW. 2015. Relative sensitivity of an amphipod *Hyalella azteca*, a midge *Chironomus dilutus*, and a unionid mussel *Lampsilis siliquoidea* to a toxic sediment. *Environ Toxicol Chem* 34:1134–1144.
25. Little EE, Calfee RD, Theodorakos P, Brown ZA, Johnson CA. 2007. Toxicity of cobalt-complexed cyanide to *Oncorhynchus mykiss*, *Daphnia magna*, and *Ceriodaphnia dubia*: Potentiation by ultraviolet radiation and attenuation by dissolved organic carbon and adaptive UV tolerance. *Environ Sci Pollut Res* 14:333–337.
26. Mahler BJ, Ingersoll CG, Van Metre PC, Kunz JL, Little EE. 2015. Acute toxicity of runoff from sealcoated pavement to *Ceriodaphnia dubia* and *Pimephales promelas*. *Environ Sci Technol* 49:5060–5069.
27. US Environmental Protection Agency. 2000. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates, 2nd ed. EPA 600/R-99/064. Duluth, MN, USA, and Washington, DC.
28. ASTM International. 2015. Standard guide for conducting laboratory toxicity tests with freshwater mussels. E2455-06 2013. In *Annual Book of ASTM Standards*, Volume 11.06. West Conshohocken, PA, USA.
29. ASTM International. 2015. Standard test method for measuring the toxicity of sediment-associated contaminants with freshwater invertebrates. E1706-05 2010. In *Annual Book of ASTM Standards*, Vol. 11.06. West Conshohocken, PA, USA.
30. Snedecor GW, Cochran WG. 1982. *Statistical Methods*. Iowa State University, Ames, IA, USA.
31. Ritz C, Streibig JC. 2005. Bioassay Analysis using R. *J Stat Softw* 12.
32. Esri Inc. 2015. Watershed task. [cited 2015 December 1]. ArcGIS. Available from: http://www.arcgis.com/home/item.html?id=8e48f6209d5c4be98ebbf90502f41077
33. Southeastern Wisconsin Regional Planning Commission. 2010. SEWRPC 2010 land use inventory. Land Use Division and GIS Division, Waukesha, WI, USA. [cited 2015 December 1]. Available from: http://maps.sewrpc.org/regionallandinfo/metadata/2010_Land_Use_Inventory.htm
34. Van Metre PC, Mahler BJ. 2014. PAH Concentrations in lake sediment decline following ban on coal-tar-based pavement sealants in Austin, Texas. *Environ Sci Technol* 48:7222–7228.
35. R Core Team. 2015. *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria.
36. Coulter TC. 2004. *EPA-CMB8.2 Users Manual*. [cited 2016 January 2]. Available from: http://www.epa.gov/scram001/models/receptor/EPA-CMB82Manual.pdf
37. Witter AE, Nguyen MH, Baidar S, Sak PB. 2014. Coal-tar-based sealcoated pavement: A major PAH source to urban stream sediments. *Environ Pollut* 185:59–68.
38. Li A, Jang J-K, Scheff PA. 2003. Application of EPA CMB8.2 model for source apportionment of sediment PAHs in Lake Calumet, Chicago. *Environ Sci Technol* 37:2958–2965.
39. Scoggins M, McClintock NL, Gosselink L, Bryer P. 2007. Occurrence of polycyclic aromatic hydrocarbons below coal-tar-sealed parking lots and effects on stream benthic macroinvertebrate communities. *J North Am Benthol Soc* 26:694–707.
40. Watts AW, Ballestero TP, Roseen RM, Houle JP. 2010. Polycyclic aromatic hydrocarbons in stormwater runoff from sealcoated pavements. *Environ Sci Technol* 44:8849–8854.
41. Mahler BJ, Van Metre PC, Wilson JT, Musgrove M, Burbank TL, Ennis TE, Bashara TJ. 2010. Coal-tar-based parking lot sealcoat: An unrecognized source of PAH to settled house dust. *Environ Sci Technol* 44:894–900.
42. Van Metre PC, Majewski MS, Mahler BJ, Foreman WT, Braun CL, Wilson JT, Burbank TL. 2012. PAH volatilization following application of coal-tar-based pavement sealant. *Atmos Environ* 51:108–115.
43. National Institute of Standards and Technology. 2009. Certificate of analysis: Standard Reference Material 1649b: Urban dust. [cited 2015 November 24]. Available from: https://www-s.nist.gov/srmors/certificates/1649b.pdf
44. National Institute of Standards and Technology. 2013. Certificate of analysis: Standard Reference Material 1650b: Diesel particulate matter. [cited 2015 November 24]. Available from: https://www-s.nist.gov/m-srmors/certificates/1650b.pdf
45. Neff JM. 2002. *Bioaccumulation in Marine Organisms: Effect of Contaminants from Oil Well Produced Water*. Elsevier, Amsterdam, The Netherlands.
46. Stout SA, Uhler AD, Emsbo-Mattingly SD. 2004. Comparative evaluation of background anthropogenic hydrocarbons in surficial sediments from nine urban waterways. *Environ Sci Technol* 38:2987–2994.
47. Chalmers AT, Van Metre PC, Callender E. 2007. The chemical response of particle-associated contaminants in aquatic sediments to urbanization in New England, U.S.A. *J Contam Hydrol* 91:4–25.
48. Bryer PJ, Elliott JN, Willingham EJ. 2006. The effects of coal tar based pavement sealer on amphibian development and metamorphosis. *Ecotoxicology*. 15:241–247.
49. Belmont P, Morris DP, Pazzaglia FJ, Peters SC. 2009. Penetration of ultraviolet radiation in streams of eastern Pennsylvania: Topographic controls and the role of suspended particulates. *Aquat Sci* 71:189–201.
50. Kim J, Lee M, Oh S, Ku J-L, Kim K-H, Choi K. 2009. Acclimation to ultraviolet irradiation affects UV-B sensitivity of *Daphnia magna* to several environmental toxicants. *Chemosphere*. 77:1600–1608.
51. Neumann NJ, Blotz A, Wasinska-Kempka G, Rosenbruch M, Lehmann P, Ahr HJ, Vohr H-W. 2005. Evaluation of phototoxic and photoallergic potentials of 13 compounds by different in vitro and in vivo methods. *J Photochem Photobiol B* 79:25–34.
52. Bommarito T, Sparling DW, Halbrook RS. 2010. Toxicity of coal-tar pavement sealants and ultraviolet radiation to *Ambystoma maculatum*. *Ecotoxicol* 19:1147–1156.
53. Kienzler A, Mahler BJ, Van Metre PC, Schweigert N, Devaux A, Bony S. 2015. Exposure to runoff from coal-tar-sealed pavement induces genotoxicity and impairment of DNA repair capacity in the RTL-W1 fish liver cell line. *Sci Total Environ* 520:73–80.
54. Ankley GT, Burkhard LP, Cook PM, Diamond SA, Erickson RJ, Mount DR. 2003. Assessing risks from photoactivated toxicity of PAHs to aquatic organisms. In Douben, PET, ed, *PAHs: An Ecotoxicological Perspective*. John Wiley & Sons, Hoboken, NJ, USA, pp 275–296. [cited 2015 October 28]. Available from: http://onlinelibrary.wiley.com/doi/10.1002/0470867132.ch15/summary
55. Brooks KM. 2004. Polycyclic aromatic hydrocarbon migration from creosote-treated railway ties into ballast and adjacent wetlands. U.S. Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI, USA.
56. Stout SA, Graan TP. 2010. Quantitative source apportionment of PAHs in sediments of Little Menomonee River, Wisconsin: Weathered creosote versus urban background. *Environ Sci Technol* 44:2932–2939.
57. Mahler BJ, Van Metre PC, Crane JL, Watts AW, Scoggins M, Williams ES. 2012. Coal-tar-based pavement sealcoat and PAHs: Implications for the environment, human health, and stormwater management. *Environ Sci Technol* 46:3039–3045.
58. Yang Y, Van Metre PC, Mahler BJ, Wilson JT, Ligouis B, Razzaque MM, Schaeffer DJ, Werth CJ. 2010. Influence of coal-tar sealcoat and other carbonaceous materials on polycyclic aromatic hydrocarbon loading in an urban watershed. *Environ Sci Technol* 44:1217–1223.
59. Covino S, Fabianová T, Křesinová Z, Čvančarová M, Burianová E, Filipová A, Voříšková J, Baldrian P, Cajthaml T. 2015. Polycyclic aromatic hydrocarbons degradation and microbial community shifts during co-composting of creosote-treated wood. *J Hazard Mater* 301:17–26.
60. Marcotte S, Poisson T, Portet-Koltalo F, Aubrays M, Basle J, de Bort M, Giraud M, Nguyen Hoang T, Octau C, Pasquereau J, Blondeel C. 2014. Evaluation of the PAH and water-extractable phenols content in used cross ties from the French rail network. *Chemosphere*. 111:1–6.

61. Boonyatumanond R, Murakami M, Wattayakorn G, Togo A, Takada H. 2007. Sources of polycyclic aromatic hydrocarbons (PAHs) in street dust in a tropical Asian mega-city, Bangkok, Thailand. *Sci Total Environ* 384:420–432.
62. Rogge WF, Hildemann LM, Mazurek MA, Cass GR, Simoneit BRT. 1993. Sources of fine organic aerosol. 3. Road dust, tire debris, and organometallic brake lining dust: Roads as sources and sinks. *Environ Sci Technol* 27:1892–1904.
63. Oda J, Nomura S, Yasuhara A, Shibamoto T. 2001. Mobile sources of atmospheric polycyclic aromatic hydrocarbons in a roadway tunnel. *Atmos Environ* 35:4819–4827.
64. Rogge WF, Hildemann LM, Mazurek MA, Cass GR. 1998. Sources of fine organic aerosol. 9. Pine, oak, and synthetic log combustion in residential fireplaces. *Environ Sci Technol* 32:13–22.
65. Schauer JJ, Kleeman MJ, Cass GR, Simoneit BRT. 2001. Measurement of emissions from air pollution sources. 3. C1–C29 Organic compounds from fireplace combustion of wood. *Environ Sci Technol* 35:1716–1728
66. Wong PK, Wang J. 2001. The accumulation of polycyclic aromatic hydrocarbons in lubricating oil over time—A comparison of supercritical fluid and liquid–liquid extraction methods. *Environ Pollut* 112:407–415.